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Heavy Metal Anomalies in Coastal Sediments of O'ahu, Hawai'i[1]

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ABSTRACT: Interelement ratios to Cr in surface samples of coastal sediments and watershed soils of Oah'u, Hawai'i, show widespread, anomalous concentrations of Pb, Cd, and Hg when compared with basalt, the ubiquitous rock type. Enrichments of these heavy metals are especially pronounced in the carbonate sands of Kahana, Maunalua, and Māmala Bays, where enrichment factors for Pb, Cd, and Hg range from 84 to 240, 67 to 180, and 43 to 72, respectively, based on samples collected in the early 1970s. Lesser enrichments of Cu, Zn, and Ni generally parallel those of Pb, Cd, and Hg in highly contaminated areas at Pearl and Honolulu Harbors, and in cultivated watershed soils. Estimated deposition rates for Pb, Cd, and Hg from three major local source categories—motor vehicle, agriculture, and volcanic—indicate that motor vehicles are by far the largest source of Pb enrichments in O'ahu soils and sediments. Widespread mercury deposition is apparently dominated by local volcanic sources, whereas Cd deposition is more evenly dispersed among the three major sources. The estimated Pb and Cd deposition rates are in reasonable agreement with their observed sediment and soil burdens in the early 1970s. The estimated Hg deposition rates are higher than necessary to explain the observed burdens for this metal, possibly as a result of soil leaching, postdepositional volatility, or Hg uptake and re-emission by biota.

THE REDISTRIBUTION OF a variety of heavy metals by human activities during the last 100 yr has been well documented in many nearshore marine deposits (Bruland et al. 1974, Erlenkeuser et al. 1974, Thompson et al. 1975, Matsumoto 1976, Matsumoto and Wong 1977, Gerlach 1981, Schmidt and Reimers 1991, Clark 1992, De Carlo and Spencer 1995, Raine et al. 1995, Spencer et al. 1995). There are, however, natural sources of heavy metals to be considered in such studies, among them lode sources (Nelson et al. 1977), volatile metals from crustal rocks (Goldberg 1976, Desaedeleer and Goldberg 1978), and volcanic emanations (Eshleman et al. 1971, Cadle et al. 1973, Siegel et al. 1973, Mroz and Zoller 1975, Buat-Menard and Arnold 1978, Siegel and Siegel 1978*a*,*b*, Zoller et al. 1983, Nriagu 1989). Of these natural sources, volcanic emanations are the most pervasive and, therefore, the closest to human activities in distribution potential. For example, Buat-Menard and Arnold (1978) estimated that, although insignificant for Pb, the contribution to atmospheric discharge from the active volcano Mount Etna is comparable in magnitude with Mediterranean anthropogenic sources for Cd, Hg, Cu, and Zn and is predominant for Se.

In Hawai'i, cases have been made for both volcanic and anthropogenic sources of mercury. While recognizing potential contributions from mercury-containing fungicides used in agriculture and from general urban sources, Eshleman et al. (1971) demonstrated the potential contribution of fumaroles lo-

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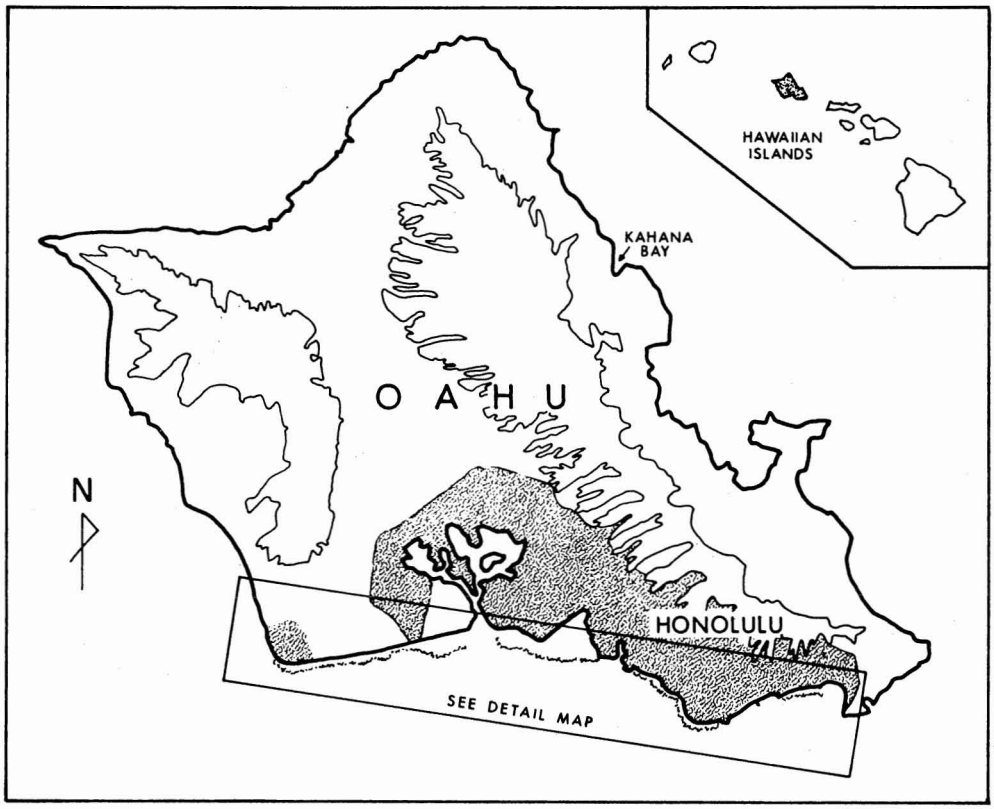

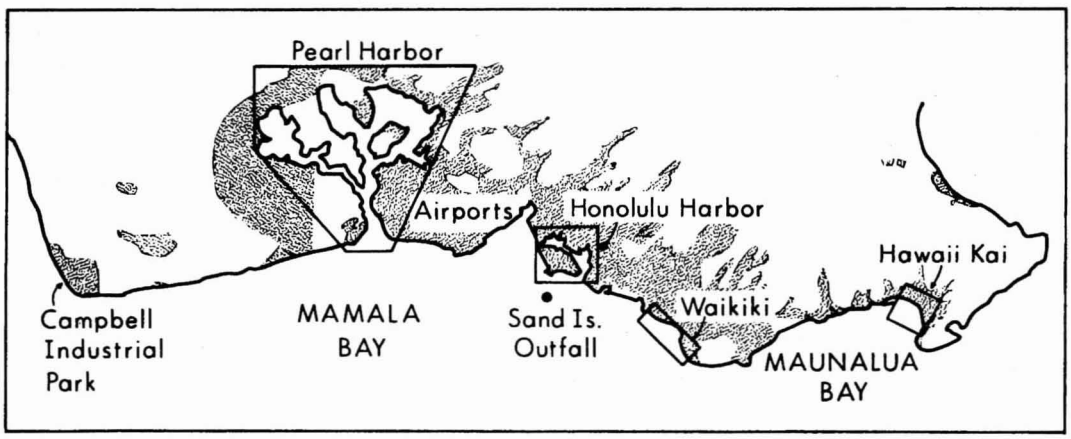

FIGURE 1. (*Top*) Index map of the island of O'ahu, Hawaiian Islands. The highly urbanized area of greater Honolulu is shaded. Approximate locations of the fringing reef ecosystems off southern O'ahu are also shown. Wind pattern is predominately northeast to southwest (NE trades). (*Bottom*) Detail map of southern O'ahu. Shaded areas are highly urbanized. Sampling areas are indicated by boxes.

cated on the active volcano Kīlauea (island of Hawai'i) to atmospheric Hg levels on the island of O'ahu. Subsequent work has reinforced the hypothesis that volcanic emissions play an important role in Hawaiian Hg dispersion (Siegel et al. 1973, Siegel and Siegel 1978*a*,*b*).

Our study interpreted data on heavy metals in nearshore sediments, stream deposits, and watershed soils of O'ahu, Hawai'i, an island that possesses potential sources of heavy metals from both its expanding population and its neighboring, active volcanoes (Figure 1). This interpretation was initiated because, despite a large number of samples analyzed for a variety of heavy metals as part of several environmental-monitoring programs on O'ahu, little, if any, interpretation of these metal concentrations was provided. This study's goals were (1) the identification of anomalous concentrations of these metals; (2) the identification of their sources; and (3) the quantification of the relative contributions of volcanic and anthropogenic sources on the island of O'ahu.

MATERIALS AND METHODS

Table 1 presents a summary of the heavy metal data for southern O'ahu soils and sediments collected by the U.S. Navy, the Water Resources Research Center of the University of Hawai'i, and the City and County of Honolulu. Sampling locations are presented in Figure 1. "Baseline" values are included for uncultivated soils and for sediments from

TABLE 1

HEAVY METAL CONCENTRATIONS IN O'AHU COASTAL SEDIMENTS AND SOILS (ppm)

LOCATION	Pb	Cu	Zn	Cd	Hg	Ni	Cr
Pearl Harbor[a]	95 (57)	127 (58)	196 (58)	1.20 (41)	1.12 (50)	62 (58)	70 (58)
SE harbor sediments	82–110	110–146	172–223	1.04–1.38	0.99–1.28	57–68	64–76
Pearl Harbor[a]	22 (40)	65 (40)	135 (40)	0.49 (14)	0.34 (32)	126 (40)	103 (40)
NW harbor sediments	20–24	57–74	122–148	0.42–0.57	0.30–0.38	106–149	91–116
Pearl Harbor[a]	26 (10)	45 (10)	80 (10)	0.75 (4)	0.47 (10)	113 (10)	99 (10)
Stream sediments	17–38	39–51	67–95	0.25–2.25	0.38–0.58	103–125	89–110
Pearl Harbor[a]	10 (7)	93 (7)	134 (7)	1.12 (7)	0.53 (7)	171 (7)	52 (7)
Cultivated soils	7.5–14	79–109	106–169	0.77–1.61	0.40–0.69	117–251	43–64
Pearl Harbor[a]	8.5 (14)	29 (15)	40 (15)	0.17 (1)	0.30 (14)	60 (15)	54 (15)
Uncultivated soils	6.6–11	24–34	35–46	—	0.20–0.45	48–75	44–67
Kahana Stream[b]	18 (7)	73 (7)	53 (7)	1.49 (4)	0.072 (5)	192 (7)	105 (7)
(NE O'ahu)	14–23	62–86	48–59	1.32–1.68	0.053–0.097	164–224	90–124
Kahana Bay[b]	26 (55)	7.9 (53)	11 (54)	1.64 (42)	0.073 (43)	36 (55)	15 (55)
(NE O'ahu)	24–27	7.0–9.0	10–13	1.52–1.78	0.061–0.086	33–39	13–17
Waikīkī Beach[b]	37 (22)	3.6 (22)	6.0 (22)	0.65 (22)	0.089 (20)	38 (21)	16 (22)
(Māmala Bay)	35–38	3.3–4.0	5.4–6.6	0.59–0.71	0.075–0.106	36–40	15–17
Hawai'i Kai[b]	32 (48)	30 (47)	44 (48)	1.82 (36)	0.13 (42)	95 (48)	39 (48)
(Maunalua Bay)	30–33	26–35	39–49	1.58–2.09	0.11–0.16	88–103	35–43
Sand Island[c]	90 (1)	8.0 (1)	25 (1)	—	0.01 (1)	—	—
Outfall	—	—	—	—	—	—	—
Kapalama Canal[c]	330 (1)	165 (1)	480 (1)	—	0.95 (1)	—	—
Honolulu Harbor	—	—	—	—	—	—	—
Scleractinian corals[d]	0.27 (26)	0.28 (26)	2.4 (26)	0.053 (26)	—	0.170 (26)	—
Poritidae	0.13–0.41	0.15–0.41	1.3–3.5	0.019–0.087	—	0.0–0.340	—

Lognormal means for the number of observations (parentheses). Range represents values within one standard error of mean. Samples did not include zero values and "not detected" results.

[a] Source: Naval Civil Engineering Laboratory (1973*a*).

[b] Source: Water Resources Research Center (1973).

[c] Source: City and County of Honolulu (1971).

[d] Source: St. John (1974). Samples consisted of pristine, unstained living coral specimens.

Kahana Bay, northeastern O'ahu, an area generally regarded to be unaffected by urbanization or agriculture (Figure 1). In general, the analytical procedures employed by these agencies used standard total digestion methods with a combination of mineral acids to release the various heavy metals for detection by atomic absorption spectrophotometry (Bernas 1968). Most report careful collection methodology before the analytical work, following guidelines of the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency 1971). Table 2 summarizes the various methods and quality assurance reported by the major contributors to the Hawai'i heavy metals database. Reported precision and accuracy for most metals are <20% relative, with the exception of a 46% relative accuracy for the Cr analyses reported by the U.S. Navy (Table 2). Inspection of the U.S. Navy standards comparison for Cr revealed a bias toward determined values higher than the "true" values, especially for the largest excursions, suggesting that the Cr-normalized results we present for this subset may be too low. The source of error in the comparison of the mean values presented in Table 1 is a combination of these analytical

TABLE 2

Summary of Heavy Metals Data Quality Assurance

PARAMETER	Pb	Cu	Zn	Cd	Hg	Ni	Cr
Naval Civil Engineering Laboratory (1973*a*,*b*)							
Analytical method used[a]	AAS	AAS	AAS	AAS	Flameless AAS	AAS	AAS
Detection limit	0.10 ppm	0.02 ppm	0.02 ppm	0.02 ppm	0.005 ppm	0.04 ppm	0.10 ppm
Precision (%)	—	—	—	—	—	—	—
Accuracy (%)[b]	12	17	13	17	—	—	46
Standards used	Daily stds., daily spiked stds., EPA stds.						
Water Resources Research Center (1973)							
Analytical method used	AAS	AAS	AAS	AAS	Flameless AAS	AAS	AAS
Detection limit	0.10 ppm	0.02 ppm	0.02 ppm	0.02 ppm	0.005 ppm	0.04 ppm	0.10 ppm
Precision (%)	—	—	—	—	—	—	—
Accuracy (%)	—	—	—	—	—	—	—
Standards used	Spiked stds., reagent stock solutions						
Herlicska (1967); this study (Table 3)[c]							
Analytical method used	GF AAS[c]	AAS	AAS	GF AAS[c]	Gold-film[c]	AAS	AAS
Detection limit	0.01 ppm	0.05 ppm	0.03 ppm	0.01 ppm	0.001 ppm	0.06 ppm	0.05 ppm
Precision (%)	7	2	<2.5	3	15	2	2
Accuracy (%)	<10	2	<2.5	22	<10	2	2
Standards used	Standard solutions from reagent-grade chlorides; std. additions, several USGS rock stds., including BCR-1 (this study)						
This study (Table 4)							
Analytical method used	AAS	AAS	AAS	AAS	Gold-film	AAS	AAS
Detection limit	0.10 ppm	0.02 ppm	0.02 ppm	0.02 ppm	0.001 ppm	0.04 ppm	0.10 ppm
Precision (%)	20	4	11	2	14	10	2
Accuracy (%)	<10	<10	<10	<10	<10	<10	<10
Standards used	Std. additions, USGS std. BCR-1						
Halbig et al. (1985)							
Analytical method used	AAS	AAS	AAS	GF AAS	—	AAS	AAS
Detection limit	0.10 ppm	0.02 ppm	0.02 ppm	0.01 ppm	—	0.04 ppm	0.10 ppm
Precision (%)	—	—	—	—	—	—	—
Accuracy (%)	—	8	11	—	—	6	10
Standards used	Commercial reagent stock solutions, std. additions, four Canadian ref. soil stds.						

[a] AAS, Flame atomic absorption spectrophotometry; flameless AAS, cold vapor technique; GF AAS, graphite furnace; gold-film, gold-film Hg analyzer.

[b] Mean relative percentage based on two runs of four EPA metal standards ($n = 8$).

[c] Analyses done in this study.

TABLE 3

HEAVY METAL CONCENTRATIONS IN HAWAIIAN VOLCANIC ROCKS (ppm)

IDENTITY	DESCRIPTION[a]	Pb[b]	Cu[c]	Zn[c]	Cd[b]	Hg[b]	Ni[c]	Cr[c]
HIGS-1	Olivine-rich pumice, Kīlauea 1959 eruption	2.9	118	115	0.21	0.021	1,200	2,006
HIGS-2	Tholeiitic basalt, Kīlauea, prehistoric[d]	5.0	126	135	0.41	0.067	181	385
HIGS-3	Trachyte obsidian, Hualālai, Hawai'i	17	21	180	0.49	0.044	2	11
HIGS-4	Quartz diabase, Ko'olau range, O'ahu[d]	4.0	167	107	0.39	0.044	218	511
HIGS-5	Melilite nephelinite, Honolulu, O'ahu	8.3	70	204	0.32	0.043	485	461
HIGS-6	Tholeiitic basalt, Wai'anae range, O'ahu[d]	4.4	156	99	0.36	0.017	401	628
HIGS-7	Rhyodacite, Wai'anae range, O'ahu	20	23	105	0.25	0.042	16	287
HIGS-8	Alkalic olivine basalt, Wai'anae range, O'ahu	4.9	111	145	0.13	0.039	237	388

[a] Hawaiian volcanic rock descriptions from Macdonald et al. (1972).
[b] Pb and Cd analyses by graphite furnace atomic absorption spectrometry. Hg analyses by gold-film Hg detector.
[c] Data from Herlicska (1967).
[d] Samples most representative of typical O'ahu basalt.

TABLE 4

HEAVY METAL CONCENTRATIONS IN HAWAIIAN AGRICULTURAL FERTILIZERS (ppm)

DESCRIPTION	Pb	Cu	Zn	Cd	Hg	Ni	Cr
Superphosphate C. Brewer Co.	25	44	1,200	72	0.029	114	634
Superphosphate Circa 1970	10	47	1,170	66	0.014	100	461
Rock phosphate	13	13	43	5.8	0.011	21	66

All analyses by flame atomic absorption spectrometry except Hg. Mercury analyses by gold-film Hg detector.

errors and the natural variability found within a sampling site, as reflected in the range represented by the standard errors.

Table 3 presents heavy metal concentrations for eight samples of Hawaiian volcanic rocks representing a range of compositions from rhyodacite to olivine basalt. Values for Cu, Zn, Ni, and Cr are taken from Herlicska (1967), who used standard atomic absorption techniques similar to those of Bernas (1968). We determined Pb and Cd values on splits of these rock samples by the Bernas (1968) technique, using an atomic absorption spectrophotometer (Perkin-Elmer model 603) and a graphite furnace (Perkin-Elmer HGA 400). The samples were dried at 110°C and digested in ultrapure mineral acids. Linear regression analysis of working curves generated by the method of standard additions yielded correlation coefficients of ≥ 0.990. Mercury was determined on air-dried splits of the samples with a gold-film Hg analyzer (Jerome Instruments) (McNerny et al. 1972). Accuracy was monitored throughout by inclusion of USGS standard basalt BCR-1 (Flanagan 1973).

The heavy metal analyses reported for the rock phosphate and superphosphates in Table 4 were determined by the techniques mentioned, under similar working conditions.

Because of their relative concentrations, flame atomic absorption spectroscopy was used. Calculated precision and accuracy estimates for these analyses are reported in Table 2.

Methods of Analysis

The soils and Pearl Harbor and Kahana stream sediments are clay-silts derived from basalt weathering (Turner 1975, Coulbourn 1971, Naval Civil Engineering Laboratory 1973*a*), whereas the nearshore sediments listed in Table 1 are largely carbonate sands derived from the fringing coral reefs with some admixture of these basaltic weathering products (Water Resources Research Center 1973). Inspection of the heavy metal content in the skeletal carbonate of pristine scleractinian corals from the family Poritidae, the most representative coral of Hawaiian fringing reefs, shows that with the exception of Zn, this material cannot account for the vast majority of the observed metal concentrations in the nearshore sediments (Table 1). It is possible to distinguish anomalous metal concentrations from those at baseline, or natural "background" levels in Hawai'i, by comparing the interelement abundance ratios of the sample to those of basalt, the essentially ubiquitous rock type. Here we have chosen two tholeiitic basalts (HIGS-2 and HIGS-6) and a quartz diabase (HIGS-4) as samples most representative of typical O'ahu basalt (Table 3). Although we display the full range of Hawaiian volcanic rock interelement abundance ratios, the HIGS sample series was chosen to represent a wide range of Hawaiian rock compositions (Macdonald et al. 1972), and many samples are not representative of the vast majority. A possible exception to those rejected on this basis are alkalic basalts, because late-stage or posterosional volcanism on O'ahu has produced this rock type and the explosive volcanism common to its occurrence has produced a relatively easily weathered source rock that could influence the soils and coastal sediments of southeastern O'ahu. Comparison of the heavy metal concentrations of HIGS-8, an alkalic olivine basalt from O'ahu, with the other three samples shows that its interelement abundance ratios are similar to those chosen as most representative of typical O'ahu basalt (Table 3).

Comparison of interelement abundance ratios assumes that no volatilization, solution, or residual concentration occurred during the weathering process. Some mobilization did occur, however, as demonstrated in Hawaiian basalt alteration studies (Palmer 1931, Payne and Mau 1946, Patterson 1971, Wilkniss et al. 1971). Volatilization and solution will decrease the magnitude of the anomalies presented below, whereas residual concentration will enhance the anomalies. It was therefore necessary to choose an element whose chemical behavior during weathering is relatively immobile, such as Al, Ti, or Cr, to normalize the rest of the elements in the sample.

Chromium was chosen for two reasons. First, it was the only element of potential residual behavior common to all data sets. Second, studies of the Cr distribution in Hawaiian weathering products and rocks indicated that Cr is indeed a residual weathering element here that can often accumulate in the soil relative to Al (Nakamura and Sherman 1958). On the other hand, more soluble or volatile elements or both, such as Pb, Cu, Ni, and Hg, tend to be removed during basalt weathering (Patterson 1971, Siegel et al. 1973). Interelement ratios to Cr should therefore yield conservative anomalies for the more mobile metals, especially if any substantial anthropogenic sources of Cr exist (e.g., Mertz et al. 1974).

RESULTS

The first step of the interelement calculations was to gather data into four groups based on localities—Pearl Harbor, Kahana, Hawai'i Kai, and Waikīkī. The Pearl Harbor and Kahana groups were further subdivided into subgroups. For Pearl Harbor, the subgroups were southeast harbor, northwest harbor, uncultivated soil, cultivated soil, and steam sediments. For Kahana, the subgroups were bay sediments and valley (stream) sediments. This resulted in the data being in nine basic sets.

We next wished to determine whether the data were homogenous enough within each of these sets to be represented by a mean with some associated error. To do this, the data from each of the nine sets were plotted as normal probability plots both directly and after having been converted to logarithms. The manipulations at this stage were greatly facilitated by the use of program P5D in the BMDP program library (Dixon and Brown 1977). In this form, the data can be compared to a normal distribution or a lognormal distribution, which has been widely found for trace element distributions in geochemical studies (McCammon 1974). A normal distribution plots as a straight line in a probability plot. The comparison can be quantified by use of the Kolmogorov-Smirnov test for goodness of fit (Massey 1951). In this test, the maximum deviation of the data from a normal distribution is compared with the expected deviation for random samples of the same size.

This test was done on seven elemental abundances for each of the nine groups. Two of the 63 groups failed the test at the 10% level against a lognormal distribution, whereas almost 20 failed the same test against a normal distribution, indicating that the elemental abundances are lognormally distributed, and they appear to be generally homogeneous. A typical histogram for Pb and its probability plot are shown in Figure 2. The data shown in Table 1 are the resulting lognormal means and standard errors for all data sets.

Because we desired interelement ratios to Cr for each group and not simple elemental abundances, the same test was performed on the six interelement ratios on the nine

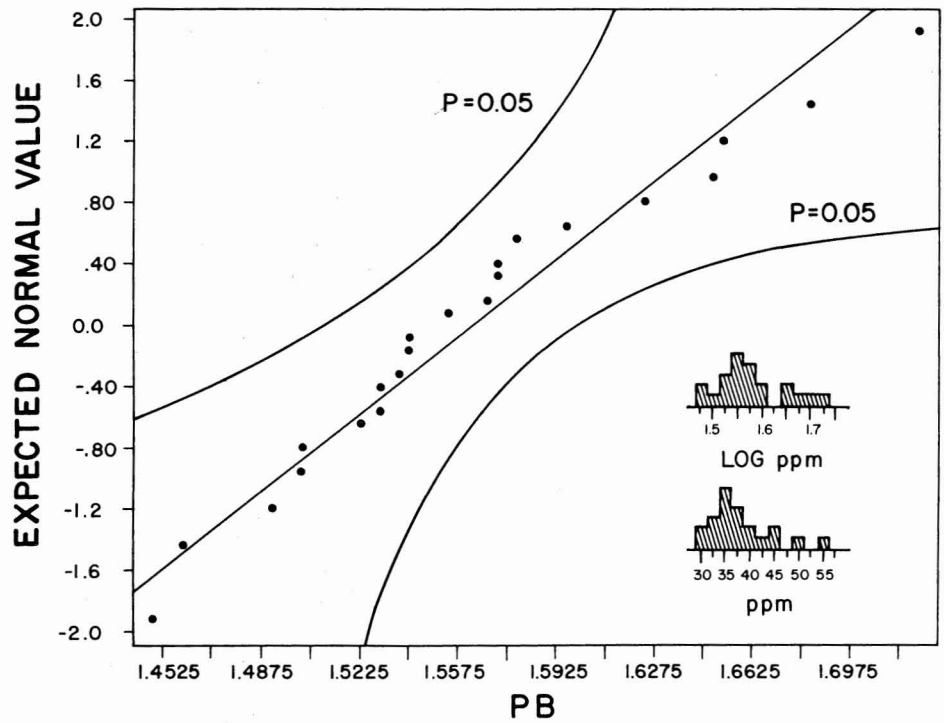

FIGURE 2. Typical graphical test of the hypothesis that the population of heavy metal values in each grouping is lognormal at the 10% level of confidence. Theoretical normal curve is indicated by the straight line. Case is for Pb values of Waikīkī Beach sediments. Insert: bottom histogram illustrates positive skewness toward higher Pb values characteristic of the lognormal distribution; top histogram of log Pb values approaches the normal distribution.

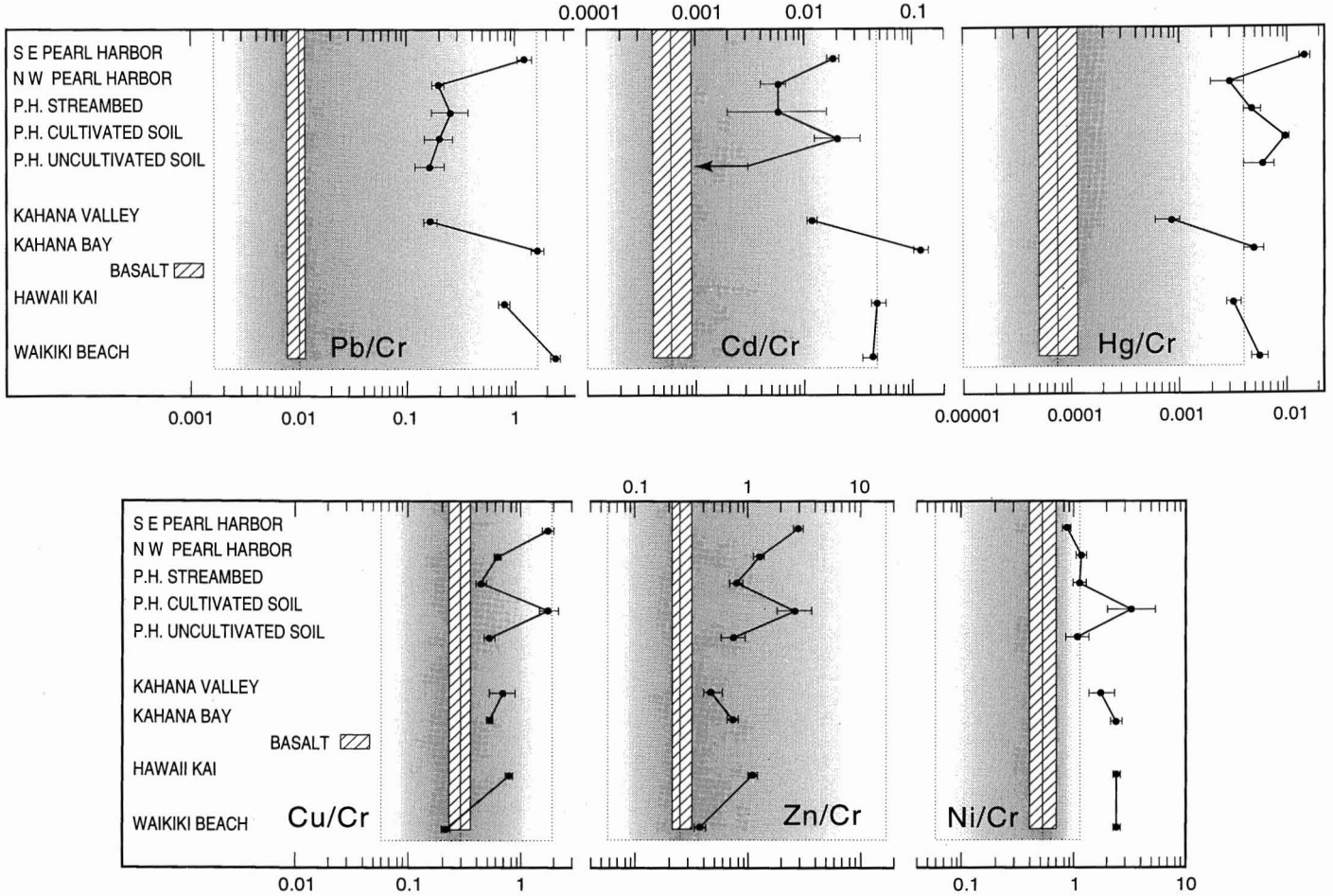

FIGURE 3. Plots of Pb, Cd, Hg, Cu, Zn, and Ni in ratio to Cr for each sampling group. Values are geometric means and their associated standard errors. Also shown for comparison is the geometric mean and standard error of the same ratio for typical O'ahu basalts (hatchured) and the full range of the ratio for Hawaiian volcanic rocks based on the data in Table 3 (shaded). Only one nonzero value was reported for the Cd/Cr ratio of the Pearl Harbor uncultivated soil, which we have taken as the upper limit of this group.

groups described. Each group was found to be consistent with the lognormal distribution of the elemental abundance. The geometric mean of these groups and their standard error are presented in Figure 3.

The comparative interelement ratios to basalt presented graphically for each element in Figure 3 are presented as enrichment factors in Table 5. The enrichment factors were calculated relative to the mean of the three samples considered representative of O'ahu basalt (Table 3) by normalizing to Cr as: EF (element X) = $(X/Cr)_{sample}/(X/Cr)_{basalt}$. These factors display the magnitude of enrichment (or depletion) of an element in a given area relative to that of basalt; a value of 1.0 reflects no enrichment or depletion. Underlined values in Table 5 are considered significant enrichments for that element relative to basalt. Generally, enrichment factors within a range of 0.2 to 5.0 around the "equilibrium" value of 1.0 are considered to be within the error of the assumptions presented above for the interelement ratios and of the group errors presented in Figure 3. Comparison of the Cr-based calculated enrichment factors for Hg and Cd in the Kīlauea fume particulates in Table 5 (Halema'uma'u Crater; Hg/Cd = 10) with those estimated for Kīlauea from particle collection at the Mauna Loa Observatory during the 1983 Pu'u 'Ō'ō eruption, where Al was used

TABLE 5

MEAN ENRICHMENT FACTORS[a] FOR O'AHU SEDIMENTS AND SOILS, HAWAI'I ISLAND SOILS, FERTILIZER, AND KĪLAUEA EMISSIONS

LOCATION	Pb	Cu	Zn	Cd	Hg	Ni
Pearl Harbor sediments						
SE harbor	140	6.2	11	28	200	1.7
NW harbor	22	2.1	5.1	7.7	42	2.3
Stream	26	1.5	3.1	12	60	2.2
Pearl Harbor soils						
Cultivated	20	6.0	10	35	130	6.2
Uncultivated	16	1.8	2.9	5.1	70	2.1
Kahana Stream sediments	17	2.3	2	23	8.7	3.5
Kahana Bay sediments	180	1.8	3	180	62	4.6
Waikīkī Beach sediments	240	0.8	1.5	67	72	4.6
Hawai'i Kai sediments	84	2.7	4.4	76	43	4.7
Hawai'i Island soils[b]						
Kohala						
HCl extract	30	2.9	4.2	11	—	1.1
Total dissol.	—	0.9	2.2	—	—	1.3
Kawaihae						
HCl extract	21	4.9	1.1	6.6	—	1.0
Total dissol.	—	0.7	0.9	—	—	1.2
Hilo						
HCl extract	45	5.1	6.1	7.4	—	2.3
Total dissol.	—	1.2	1.5	—	—	1.7
Superphosphates[c]	3.3	0.3	8.4	200	0.5	0.4
Kīlauea fume particulates[d]	71	15	—	240	2,400	0.0
Kīlauea fumarole condensates[e]	—	4.2	360	—	—	—

[a] Enrichment factors calculated relative to mean of three samples considered representative of O'ahu basalt (Table 3) by normalizing to Cr as: EF (element X) = $(X/Cr)_{sample}/(X/Cr)_{basalt}$. Underlined values are considered significant (see text).

[b] Source: Halbig et al. (1985). Nonresidual metals extracted with 0.5 N HCl. For these data, normal distribution means were used; the number of samples in each locality ranged from 20 to 28 for HCl extractions and from 10 to 21 for total dissolutions.

[c] Calculated from average of superphosphate analyses in Table 4.

[d] Collected from Halema'uma'u Crater; Zn not determined (Cadle et al. 1973).

[e] Collected from Halema'uma'u Crater; from single sample with all values above detection limits (no. 9) (Barnard et al. 1990).

as the basalt baseline normalization agent, shows a very similar ratio but absolute differences of 10^3 (Zoller et al. 1983) that is probably attributable to eruptive activity over less-active, steady-state fumarolic degassing (Cadle et al. 1973).

DISCUSSION

General Observations

Inspection of the data in Tables 1 and 5 and of Figure 3 indicates that major anomalies exist for the metals Pb, Cd, and Hg. Lead values higher than the basalt baseline value occur widely and are highest in southeastern Pearl and Honolulu Harbors, and near the Sand Island sewer outfall (Figure 1). With the exception of the Sand Island sewer outfall, enrichment trends for Cu, Zn, Cd, and Hg generally parallel those of Pb in these areas. The major source of the anomalous Pb concentrations is probably anthropogenic Pb that is introduced from both local (Eshleman 1973, De Carlo and Spencer 1995, Spencer et al. 1995) and long-range sources (Hoffman et al. 1972, Spencer et al. 1995). Pb originates from the combustion and aeolian distribution of tetraethyl lead added to automobile gasolines since 1945 (Chow et al. 1973). That the Pb anomalies presented here are widespread also implies an aeolian distribution of the Pb, although the concentrations seen for Pearl and Honolulu Harbors indicate point sources that are probably related to the naval industries there. Another point source at the Sand Island sewer outfall may also be caused by industrial wastes.

Comparison of the cultivated and uncultivated Pearl Harbor soils shows that cultivation apparently has a large effect on the level of Cd, as well as some effect on the levels of Zn, Cu, Ni, and Hg (Figure 3 and Table 5). The Cd enrichment is likely even more pronounced than indicated, considering that the lognormal means used in Table 1 have precluded incorporation of 14 out of 15 uncultivated soil samples that were below the detection limit (0.02 ppm, Table 2). Possible sources for these concentrations are agricultural fertilizers, fungicides, and herbicides used primarily in the sugarcane and pineapple industries. Rock phosphates and especially superphosphates contain large amounts of Cd and Zn as impurities, although these fertilizers are not considerably enriched in the other metals relative to basalt (Tables 3 and 4). Organo-mercuric fungicides are a potentially large source of Hg, and analogs based on other metals or herbicides may be the source of Cu and Ni enrichments. Nevertheless, continued use of these highly soluble materials over time will lead to a buildup in the soil, as pointed out by Barrows (1966) and demonstrated for Zn in superphosphate-treated Hawaiian soils (Saeed and Fox 1978).

The Kahana Valley stream samples show heavy metal ratios to Cr that, with the exception of Cd and Hg, are generally closest to those of the Pearl Harbor uncultivated soil and stream samples. With the further exception of Pb, these values may reflect the local basalt baseline for that area (Figure 3 and Table 5). Also included in Table 5 are calculated enrichment factors for soils from relatively pristine sites on the less-populated island of Hawai'i (Halbig et al. 1985). These data generally support the notion that enrichment factors within about 0.2 to 5.0 probably reflect the local basalt baseline. With the exception of Ni, enrichment factors for the 0.5 N HCl extracts of the Hawai'i Island soils are consistently higher than the total dissolutions; these likely reflect Cr partitioning into more residual phases relative to the other metals, because only about 5% of the total Cr was extracted (Halbig et al. 1985). Chromium partitioning probably explains at least part of the relatively large enrichment factors for Pb and Cd; comparison of the HCl-extracted enrichment factors with those for total dissolutions of Cu and Zn suggest 2- to 7-fold enhancements of the HCl-extracted enrichment factors. However, there may be a mechanism behind the residual Hawai'i Island soil Pb and Cd enrichments. Of the three soil sampling sites, only Hilo contains substantial cultivation (Halbig et al. 1985). Although less populated than O'ahu, all sites contain well-traveled highways. Unfor-

tunately, no companion Hg determinations were made that would help constrain the possible enrichment sources.

Comparison of the Kahana Valley stream sediments with the Kahana Bay samples (Figure 3) shows marked differences in the Pb, Cd, and Hg ratios and enrichment factors (Table 5). This is in contrast to the Pearl Harbor area, where from the uncultivated watershed soils into the relatively uncontaminated northwest harbor no ratio changes markedly. A major difference between these areas is their comparative watershed-bay lithology; the harbor sediments are essentially the same clay-silts as the soils (Turner 1975), whereas the Kahana Bay sediments are largely carbonate sands (Coulbourn 1971). Other sites of the same carbonate sand lithology (Water Resources Research Center 1973) and the same large anomalies in their Pb, Cd, and Hg ratios are Hawai'i Kai (Maunalua Bay) and Waikīkī (Māmala Bay), with Waikīkī displaying the largest Pb anomaly.

Although not completely clarified on the basis of the existing data, three possible explanations for the apparent Pb, Cd, and Hg enrichments in the carbonate sands are as follows: (1) differential transport of Pb, Cd, and Hg relative to Cr. Although this mechanism is consistent with the relative solubilities of these metals, it is inconsistent with the short-range readsorption of Pb in clays (Patterson 1971) and with known levels of particulate transport into the bays (Coulbourn 1971); (2) preferential uptake in the carbonate sediments. The affinity of Hg and Cd for organic matter is well documented (Siegel et al. 1975, Gong et al. 1977), as are the organic matter associations of recent carbonate sediments (Suess 1973). The uptake of Pb, Cd, and Hg from surface seawater by marine organisms has been suggested (Rama et al. 1961, Knauer and Martin 1972, Bender and Gagner 1976), although Pb is generally thought to be associated with inorganic particulates (Turekian 1977); (3) proximity to localized anthropogenic sources. The Kahana, Maunalua, and Māmala Bay areas are in close proximity to major highways. This observation can readily explain the large Pb anomalies in the carbonate sediments and may also explain the elevated Cd and Hg levels. Eshleman (1973) and Siegel and Eshleman (1975) reported elevated Hg levels that parallel those of Pb near major highways on O'ahu. Elevated levels of Cd, which parallel those of Pb, have been reported in roadside soils by Lagerwerff and Specht (1970). These correlations are illustrated in Figure 4. Contributions of Hg from marine antifouling paints used in the late 1950s to early 1970s have been demonstrated for sediments from the Ala Wai Canal and Yacht Harbor (Raine et al. 1995). Mercury from this source is

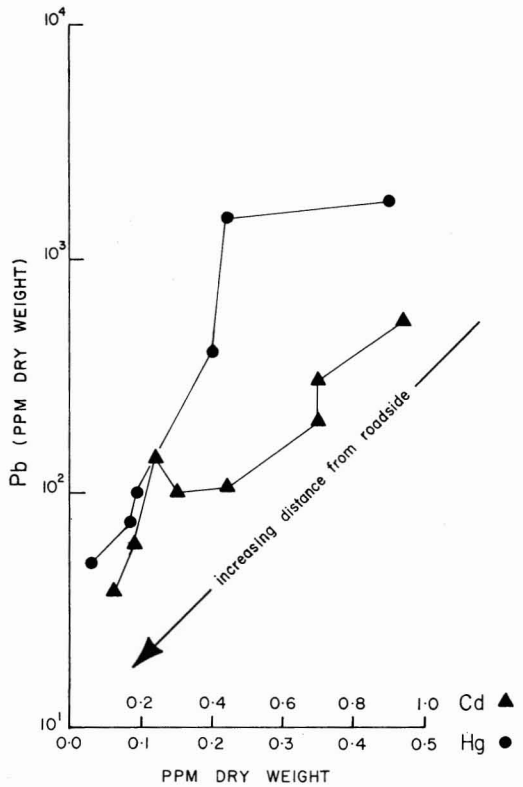

FIGURE 4. Pb-Hg and Pb-Cd relationships in roadside soils. Pb-Hg data collected on a traverse perpendicular to Ala Moana Boulevard, Honolulu. Estimated traffic volume at time of collection was 60,000 units per day (Eshleman 1973). Pb-Cd data collected on a traverse perpendicular to Baltimore-Washington Parkway, Bladensburg, Maryland. Estimated traffic volume at time of collection was 48,000 units per day (Lagerwerff and Specht 1970).

likely to predominate in sediments beneath relatively restricted and heavily navigated waters such as harbors and marinas.

Volcanic Versus Anthropogenic Contributions to Burdens of Hg, Cd, and Pb

The sources of Hg and Cd in Hawaiian soils and sediments can be classified as: (1) volcanic emissions, including fumaroles, eruptions, and lava flows; (2) baseline basalt, including lode sources associated with ancient volcanic centers; (3) fertilizers and, for Hg, organo-mercuric fungicides used in agriculture; and (4) general urban and industrial uses (e.g., Hg in chlorine bleaches [Siegel and Eshleman 1975] and electro-chemical products, as well as possible automotive emissions). Lead also has origins from these various sources, although its major source in automotive emissions has been well documented (Chow et al. 1973, Eshleman 1973). An attempt to quantify the relative contributions of the major sources of anomalous Hg, Cd, and Pb levels on O'ahu is presented in Table 6. The three major contributors relative to baseline basalt values of these metals are classified as motor vehicle, agriculture, and volcanic. Industrial sources have been omitted because: (1) they are not highly developed on O'ahu; (2) documentation is difficult; and (3) their effects, although sometimes considerable, are generally localized. The rationale for the calculation of the relative contributions in Table 6 is presented below.

The deposition rates for motor vehicle Pb on O'ahu were calculated from gasoline consumption figures provided by the State Department of Taxation, and the relative percentages of the three major grades (premium, regular [or low lead], and unleaded) were provided by the State Energy Branch (Department of Business and Economic Development). The range of Pb values represents the change in the relative percentages of these three major grades since the introduction of unleaded gasolines in 1970. Annual leaded gasoline consumption peaked on O'ahu in 1971 (maximum estimate, Table 6), and the 1979 figures (minimum estimate, Table 6) are similar to those of the early 1950s (Figure 5).

Mercury and Cd contributions from motor vehicles were estimated from their respective mean ratios to Pb in roadside soils (Figure 4). Most of the Pb that originates from motor vehicles is in the form of tetraethyl lead gasoline additives. The vehicular origins

TABLE 6

Estimated Contributions to O'ahu Deposition Rates of Pb, Hg, and Cd for the Period 1953 to 1979 (μg/kg yr)

ELEMENT	AREA	MOTOR VEHICLE	AGRICULTURE	VOLCANIC[a]	TOTAL
Pb	All O'ahu[b]	215–475	0.18–0.43	**3.3**–13	218–488
	Agriculture[c]	215–475	1.3–3.3	**3.3**–13	220–491
	Urban[d]	1,575–3,500	0.18–0.43	**3.3**–13	1,580–3,513
Hg	All O'ahu	0.13–0.30	<0.03–3.3	1.3(**13**)–42	1.5–46
	Agriculture	0.13–0.30	<0.03–23	1.3(**13**)–42	1.5–65
	Urban	1.0–2.2	<0.03–3.3	1.3(**13**)–42	2.3–48
Cd	All O'ahu	0.60–1.3	0.10–1.3	**0.83**–3.9	1.5–6.5
	Agriculture	0.60–1.3	0.75–9.0	**0.83**–3.9	2.2–14
	Urban	4.3–9.5	0.10–1.3	**0.83**–3.9	5.2–15

Calculated assuming containment in upper 60 cm of soil with average density of 1.0 g/cm^3; 1 km^2 = 6 × 10^8 kg (after Siegel and Siegel 1978*b*). Similar deposition rates may extend beyond this period for Hg, Cd, and nongasoline Pb sources.

[a] For volcanic sources, the minimum deposition rate is based on particulate fluxes (Cadle et al. 1973, Nriagu 1989). For Hg, value in parentheses assumes that >90% of Hg in the near-field plume is nonparticulate (Siegel et al. 1973). Boldface numbers are best estimates; see text for discussion.

[b] Total area = 1,574 km^2 (Armstrong et al. 1973).

[c] Total area = 218 km^2 (66% sugarcane, 34% pineapple).

[d] Total area = 219 km^2 (Greater Honolulu, Figure 1).

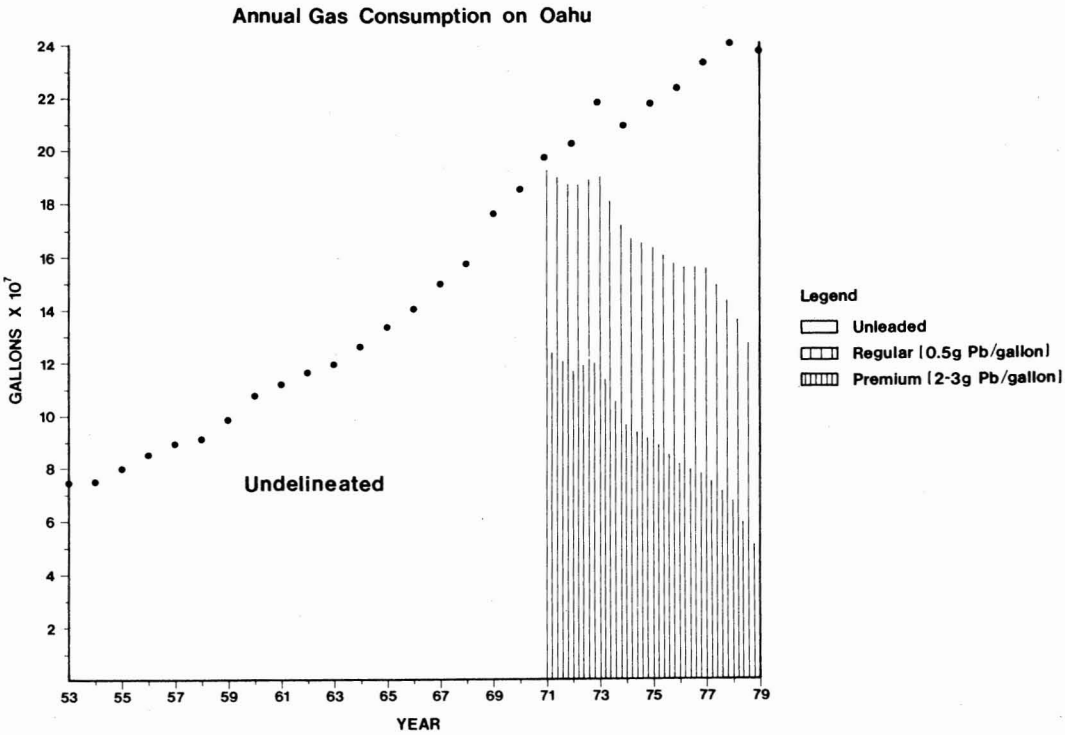

FIGURE 5. Total annual gasoline consumption on O'ahu for period from 1953 to 1979, with relative amounts of premium, regular (or low lead), and unleaded gasoline indicated. Figures from Hawai'i State Department of Taxation.

of Hg and Cd are less clear. Mercury values in 88 samples of Canadian unrefined petroleum ranged from <2 to 400 ppb, averaging 51 ppb (Hitchon et al. 1975). Much higher values of Hg have been reported in fuel (10 ppm [Bertine and Goldberg 1971]) and crude oils (19 to 21 ppm [D'Itri and D'Itri 1977]). Ten samples of crude oil from the United States and Libya exhibited a very large range from 23 to 30 ppm Hg (Shah et al. 1970). Similarly, Cd values in nine crude oils ranged from 0.26 to 27 ppb, with values of 225 and 1600 ppb found in two asphaltenes (Filby and Shah 1973). Cd in various refined oils was found to range from 0.07 to 0.54 ppm (Lagerwerff and Specht 1970). These levels may not, however, represent those of refined gasolines. Lagerwerff and Specht could not detect Cd (<0.01 ppm) in 12 brands of gasoline tested. On the other hand, those workers found Cd levels from 20 to 90 ppm in four brands of automobile tires, which suggests that at least the Cd/Pb relation may be an indirect one. Further, the calculated Hg and Cd contributions from motor vehicles based on roadside accumulations are probably minimum values because of the larger volatilities of these metals relative to Pb.

The range for agricultural deposition was calculated from an estimate of 1.65×10^7 kg for the mean annual phosphate fertilizer consumption on O'ahu from 1971 to 1980 (U.S. Department of Agriculture 1980) and from the respective ranges for Pb and Cd in rock phosphate and superphosphate of 10–25 ppm and 6–72 ppm (Table 4). Minimum Hg deposition rates were similarly calculated, using an average of ca. 20 ppb for fertilizers from Table 4. Maximum Hg deposition rates were derived from figures for organo-mercuric fungicides used in sugarcane production from 1964 through 1969 (State Department

of Agriculture 1969). Use of these fungicides was terminated in the early 1970s (S. Ching, Hawai'i Sugar Planters' Association, pers. comm.).

The range for volcanic Hg deposition on O'ahu was estimated by two approaches. First, Siegel and Siegel (1978*b*) directly measured Hg deposition on O'ahu by collection of fallout onto Cu and Au metal foils. They interpreted their values to primarily represent deposition from distal, active sources on Kīlauea Volcano, because industrial pollution sources on O'ahu are minimal and deployment of the same Hg collection devices on Kīlauea (Sulfur Banks fumarole site) gave very high deposition ($>10^2$ enrichments over O'ahu rates). Companion values for volcanic Pb and Cd deposition were calculated from the mass ratios of Pb and Cd to Hg in particulates collected in fume studies of Halema'uma'u Crater, Kīlauea Volcano (Cadle et al. 1973), and the median measured Hg deposition rate, allowing that 90% or more of the Hg emissions from Kīlauea are nonparticulate (Siegel et al. 1973). We interpret these rates as maximum values, because urban, agricultural, and other possible sources such as marine air are not delineated by the fallout collection. Volcanic mercury concentrations from past activity on O'ahu are also present that could degass and redeposit Hg, but these areas are largely confined to the ancient volcanic centers at Kailua (Souto 1978) and Wai'anae (Cox et al. 1979). Further, in a companion study, Siegel and Siegel (1978*a*) found that air Hg concentrations at the Kalalua eruption site on Kīlauea were $>10^3$-fold enriched relative to an air Hg concentration "pulse" detected on O'ahu, ca. 380 km away. This observation suggests that a much greater dilution of the air Hg concentration occurred during a seemingly more favorable transport condition (eruption and light, varied trade wind conditions more favorable for lower tropospheric plume transport toward O'ahu) (Siegel and Siegel 1978*a*).

The second approach utilized median metal/S ratios computed for the worldwide emissions from volcanoes (Nriagu 1989) and the annual S flux of 1.7×10^{11} g/yr estimated for Kīlauea from 1956 to 1983 (Gerlach and Graeber 1985). Although compiled from a variety of volcanoes, these metal/S ratios compare very well with those determined for Kīlauea fume particulates (Cadle et al. 1973). To estimate the annual deposition on O'ahu from a Kīlauea source, we decreased the computed annual metal fluxes for Kīlauea by a factor of 2.5×10^{-1} to account for a maximum of about 50% favorable wind conditions (light, varied E-NE trade winds or S "kona" winds) (T. A. Schroeder, pers. comm.) and a maximum of about 50% favorable deposition conditions (rainfall, which is much more effective than dry fallout in removing fine plume particles) (A. D. Clarke, pers. comm.). This product was multiplied by the dilution factor found for atmospheric Hg arriving at O'ahu during the Kalalua eruption ($<6 \times 10^{-4}$). Steady-state deposition is assumed. Because these rates are based on particulate emissions, the results in Table 6 are considered a minimum value for Hg, because in the near-field plume where most of these measurements were made, >90% of the Hg emissions from Kīlauea are nonparticulate (Siegel et al. 1973). For less-volatile Pb and Cd, however, these estimates are considered more reliable.

Table 6 shows that motor vehicles are by far the largest source of Pb enrichments in O'ahu soils and sediments, in agreement with previous work on Pb in the environment. Volcanic and agricultural sources supply at most 3% and 0.7% to the total Pb burdens of all O'ahu and agricultural areas, respectively (Table 6). Mercury deposition, on the other hand, is predominately volcanic. Maximum Hg contributions from agriculture and motor vehicles to the total Hg burden are 35% and 43% for agricultural and urban areas, respectively. Deposition from these sources may be considerable in localized areas within the general agricultural and urban districts, however. Cadmium deposition is the most dispersed among the three major source categories. Volcanic Cd deposition is largest (55–60%) for all O'ahu, but diminishes in importance in agricultural (28–38%) and urban areas (16–26%). Agricultural sources may supply up to 64% of the total Cd burden

in agricultural areas, whereas motor vehicles may supply up to 83% of the total Cd burden in urban areas.

Comparison of the Pb concentrations in Table 1 with the Pb deposition rates in Table 6 indicates that the estimated Pb rates are of reasonable magnitude. For example, the Waikīkī Beach mean value of 37 ppm represents an excess of greater than 36 ppm over that expected from basalt weathering, based on the respective mean Pb/Cr ratios for these samples and those of basalt (Tables 1 and 2). With a Pb deposition rate of between 1600 and 3500 ppb/yr (Table 6), the total Pb deposited from motor vehicles in the 25-yr period from 1945 to 1970 yields an excess concentration of between 40 and 88 ppm, a range from similar magnitude to about twice the excess mean Waikīkī Beach value.

When a similar comparison is made with the mean Hg concentrations in Table 1, the Hg deposition rates appear higher than expected. For example, the Waikīkī Beach excess Hg value of 88 ppb would require about 70 yr of minimum Hg deposition, but only 7 yr of deposition at our best estimated rate. Volcanic Hg deposition from distal sources, although sporadic, has likely continued over the tens of thousands of years since the cessation of volcanic activity on O'ahu. Most soils and nearshore sediments are not static accumulators, however, especially for volatile metals such as Hg. The age of the soil and sediment is another factor. The most probable explanation is either soil leaching, postdepositional volatility (e.g., Goldberg 1976), or Hg uptake and re-emission by biota, including covering vegetation (Siegel et al. 1975) and marine organisms (Knauer and Martin 1972).

The motor vehicle Cd deposition rates, if linked to gasoline additives like Pb, appear to be inadequate to explain the concentrations in Table 1. Twenty-five years of maximum Cd deposition in urban areas on O'ahu could only produce an excess Cd concentration of 375 ppb, compared with a Waikīkī Beach mean excess of about 640 ppb. However, if vehicular Cd is related more to tire wear, longer accumulation periods of up to 50 yr (ca. 1920 to 1970) would yield a maximum excess Cd concentration (750 ppb) that compares with the Waikīkī Beach mean excess value. Two hundred years of agricultural Cd deposition would produce a concentration of between 440 and 2800 ppb, compared with a mean excess Cd value of 1100 ppb for cultivated soils (Table 1). As mentioned above, the Cd deposition rates for motor vehicles are probably minimum values because of the larger volatility of Cd relative to Pb. Suspected Cd additions in the zincing of sugarcane have not been included in the agricultural source. The volcanic Cd deposition rate may be underestimated as well. The Cd/Pb mass ratio in fume particulates (Cadle et al. 1973, Buat-Menard and Arnold 1978, Nriagu 1989) is lower than that expected from the relative volatilities of these metals, assuming total retention in the particulate phase. This suggests the possible existence of nonparticulate forms of volcanic Cd. Nevertheless, even a particulate volcanic Cd deposition rate of about 1 ppb/yr could, over thousands of years, add sufficient Cd to account for the observed burdens if there were no subsequent losses through the activities of organisms or solution.

CONCLUSIONS

A comparison of interelement weight ratios to Cr with baseline basalt values has identified anomalous concentrations of Pb, Hg, and Cd in coastal sediments and watershed soils of O'ahu, Hawai'i. Lesser enrichments of Cu, Zn, and Ni generally parallel those of Pb, Hg, and Cd in highly contaminated areas associated with the naval industries at Pearl and Honolulu Harbors and with the cultivation of watershed soils.

Widespread, anomalous concentrations of Pb, Cd, and Hg occur in the carbonate sands of Kahana, Maunalua, and Māmala Bays. Of the possible explanations presented here—(1) differential transport of Pb, Cd, and Hg relative to Cr; (2) preferential uptake of Pb, Cd, and Hg in the carbonate sediments; and (3) proximity to localized anthropogenic sources—the proximity of these areas to major highways suggests that the most likely source has been motor vehicle emissions, although volcanic and agricultural sources may

also have contributed to the observed excess concentrations, as well as marine antifouling paint contributions for Hg.

Estimated deposition rates for Pb, Hg, and Cd from the three major source categories—motor vehicle, agriculture, and volcanic—indicate that motor vehicles have been by far the largest source of Pb enrichment in O'ahu soils and sediments. Hg deposition is predominately volcanic in origin, but is rivaled by agriculture and urban activities in their respective domains. Cd deposition is dispersed more evenly among the three major source categories. The calculated Pb deposition rates of 1600–3500 ppb/yr for the 25-yr period from 1945 to 1970 are in reasonable accord with the observed excess concentrations of this heavy metal in sediments near urban areas during the early 1970s. A Hg deposition rate of 13 ppb/yr (best estimate) is higher than expected from the observed concentrations, whereas Cd deposition rates of 2–15 ppb/yr, although likely underestimated, are in reasonable agreement with the observed early 1970s concentrations. Possible explanations for the disparity between the observed and calculated Hg deposition include soil leaching, postdepositional volatilization, and Hg uptake and re-emission by biota.

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